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Process for reducing Content of Sulphur compounds and Poly-aromatic Hydrocarbons in a Hydrocarbon Feed

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BACKGROUND OF THE INVENTION

The present invention relates to a process for removal of sulphur and polyaromatic compounds in vacuum gas oil by hydrotreatment of FCC hydrocarbon feed stock.

Many countries are tightening specifications for the sulphur content in diesel and gasoline fuels. The fluid catalytic cracking (FCC) units are a major source of gasoline, but also the major source of sulphur in gasoline and diesel fuels. Lower sulphur content in fuel requests either treating the FCC feed or treating its products.

Treating the FCC products involves multiple process solutions: naphtha treating, light-cycle oil (LCO) treating and flue gas treating to control the SO_x emissions. Treating feed to the FCC unit can increase yields and at the same time lower sulphur levels in gasoline, and diesel fuels and reduces SO_x emissions. The increased conversion in the FCC unit resulting from feed treatment may improve refinery margins. Product treatment, however, offers no yield benefits.

It is, thus, a general object of the invention to improve production of a FCC feed being substantially reduced in content of sulphur and nitrogen compounds and in particular having a low content of polyaromatic hydrocarbons and thereby improved crackability and conversion and selectivity in the FCC unit.

Description of Prior Art

Hydrotreatment of FCC feed substantially reduces sulphur content of gasoline, light (LCO), and decant oil. It also

lowers the amount of sulphur in spent catalyst coke, which results in the reduction of SO$_x$ emissions from the regenerator. For most feedstocks moderate to high severity hydrotreating can be used to achieve a high level of desul-

5 phurization (>90%) and greatly reduce the sulphur content of the FCC products. High severity desulphurization would be needed to reduce coke sulphur to the near zero level.

It is well known that removal of nitrogen from FCC feed

10 yields the benefits of increasing conversion and product yields. Nitrogen compounds poison the active sites in the FCC catalyst and increase coke-making propensity of the catalyst and reduce the yield of valuable products. Nitrogen removal by hydrotreatment is much harder than sulphur

15 removal. Moderate to high severity is generally required to achieve a high denitrogenation level (>70%).

Poly-aromatic hydrocarbons (PAH) do not crack in a FCC unit, but instead undergo condensation reactions to form

20 coke. PAH are defined as fused multiring aromatic compounds containing two or more aromatic rings. The concentration of PAH can be measured by the analysis method IP 391. Hydrotreating can saturate PAH and form naphthenes and paraffin compounds, which are more easily cracked in the FCC.

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This improves conversion and product yields. Mono-aromatics another product of PAH hydrogenation resist cracking in a FCC unit, but lose side chains and produce high-octane components in the FCC gasoline.

Di-aromatic species distribute in all liquid products from the FCC and also convert to coke on the FCC catalyst. Tri-aromatic and tetra-aromatic species either convert to coke on the catalyst or distribute in the light cycle oil or heavier fraction from the FCC. Maximising FCC gasoline and lighter valuable products requires an understanding of how to maximise the conversion of multiple ring aromatic species (di+) to single (mono) aromatic or saturated ring species in the FCC feed hydrotreater.

The degree of aromatic saturation is highly dependent on hydrogen partial pressure, catalyst type and the space velocity of the hydrotreater. The kinetic and thermodynamic responses of sulphur, nitrogen and other contaminant removal are such that an increase in temperature results in conversion of these contaminants. The kinetic responses for these contaminants represent irreversible reactions.

Typical conditions for a FCC pre-treatment reactor are hydrogen pressure of 40-120 bar; average reactor temperature 350-410°C; liquid hourly space velocity (LHSV) of 0.5-2.5 m^3oil/m^3catalyst/h. The exact conditions will depend on the type of the feedstock, the required degree of desulphurisation and the desired run length. The reactor temperature on fresh catalyst (start of run) is normally at the lower end of the above range and as the catalyst deactivates the reactor temperature is raised to compensate for loss of catalyst activity.

The end of the run is normally reached when the design temperature for the reactor is reached, which is decided by the metallurgy of the reactor. The lower the start of run

temperature and the higher the end of run temperature the longer the catalyst run length for a given rate of deactivation. For a refiner, the run length is a very important consideration. A shorter run length means high costs due to

5   a higher rate of catalyst replacement, and relative more downtime (i.e. time off-stream) for catalyst change-out with a resultant loss of revenue due to reduced production of high quality FCC gasoline products.

10 Further restriction on run length may be imposed, if the FCC unit operations need a reduction in poly-aromatic hydrocarbon content in addition to the reduction in sulphur and nitrogen. PAH compounds reacts readily at hydrotreating conditions. Tetra-aromatic and tree-ring aromatic compounds

15 are hydrogenated to mono-aromatic compounds. The mono-aromatic compounds react slowly at typical FCC pre-treatment conditions to form naphthenes.

The reactions are reversible and at high reaction tempera
20 tures and low hydrogen pressure the conversion of the PAH compounds is thermodynamically limited by equilibrium. Consequently, the conversion of PAH compounds in a FCC pretreatment unit producing low sulphur and nitrogen feed to the FCC unit might at first increase as reaction tempera
25 ture is increased, and then decrease as temperature is increased further owing to equilibrium constraints at the high temperature.

The aromatic saturation will pass through a maximum as the
30 reaction temperature is increased. The maximum is identified as the point, where the net rate of aromatic satura-

tion is zero due to the effects of the forward and reverse
reactions.

5 The temperature at which the PAH equilibrium is met will
depend on a number of factors including hydrogen pressure,
feed PAH content and composition and LHSV.

It is, thus, the general object of the invention to provide
a process for the production of a low sulphur and nitrogen
10 FCC feed with a low content of polyaromatic hydrocarbons
and thereby increase the FCC yields and in particular the
FCC gasoline production.

SUMMARY OF THE INVENTION

15 The present invention is a process for reducing content of
sulphur compounds and poly-aromatic hydrocarbons in a hy-
drocarbon feed stock having a boiling range between 200°C
and 600°C, which process comprises the steps of:
(a)   contacting the feed stock with hydrogen over a
20 hydrotreating catalyst at conditions being effective in hy-
drotreating and obtaining a hydrotreated effluent with the
hydrotreated feed stock, hydrogen sulphide and hydrogen;
(b)   cooling the effluent; and
(c)   contacting the effluent with a hydrotreating
25 catalyst at conditions being effective in hydrogenation of
polyaromatic hydrocarbons.

By the inventive process, a low PAH content is achieved in
FCC feeds with only slight additional investment in reactor
30 volume and without reduction in run length. The essences of
the inventive process consists of cooling the effluent ex-
iting the hydrotreating reactor and passing the cooled

product through a small posttreat reactor containing a suitable catalyst. The PAH content of the product existing in the hydrotreating reactor is reduced in the posttreatment reactor owing to the more favourable equilibrium conditions at the lower temperature. Consequently, the end of run temperature in the main hydrotreating reactor is not limited by the PAH content of the product exiting the main reactor, and a small overall reactor volume (main hydrotreater plus post treat reactor) is required for a given run length. In another embodiment of the process, the final bed of the main hydrotreating reactor is operated at lower temperature instead of using a post treatment reactor. The process can be used to lower the content of poly-aromatic hydrocarbons and thereby improve the performance of the FCC unit because of improved crackability of the FCC feed as well as the FCC product qualities.
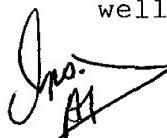
DETAILED DESCRIPTION OF THE INVENTION

The petroleum vacuum distillates used in the present invention boil in the range 400-650°C and have a PAH content in the range 5-50 wt%. Examples of petroleum fractions include straight run vacuum gas oils from a vacuum crude distillation and vacuum fractions of the product from fluid catalytic cracking and thermal cracking processes including cooking and mixtures thereof. The process is particularly suitable for blends of vacuum distillates containing thermal cracked oils and FCC products because these oils generally have a high PAH content.

The process layout is illustrated in Fig. 1. Feedstock is mixed with hydrogen, heated in the furnace 1 and passed

through the hydrotreating reactor 2. The conditions used in the hydrotreating reactor are the same as those normally used for hydrotreatment of FCC feeds, i.e. typical hydrogen pressure=40-120 bar; typical average reactor temperature

5 =340-410°C; typical LHSV=0.5-2.0 m^3oil/m^3catalyst/h and typical hydrogen gas to oil ratio=100-1000Nm^3/m^3.

The effluent from the hydrotreater is cooled to a suitable temperature by heat exchange with the feed to hydrotreater 3 or by other means before passing to post-treatment reac-

10 tor 4. The temperature employed in the post-treatment reactor will typically be in the range of 300°C to 375°C, and will typically be at least 50°C lower than the outlet temperature of the hydrotreater. The LHSV in the posttreatment reactor will typically be in the range 2-20

15 m^3oil/m^3catalyst/h and the total pressure will be at the same level as that in the hydrotreating reactor. The catalyst used in the hydrotreating reactor may be any catalyst used for hydrotreating petroleum fractions and known in the art. The catalyst contains at least one metal on a porous

20 refractory inorganic oxide support. Examples of metals having hydrotreating activity include metals from groups VI-B and VIII e.g. Co, Mo, Ni, W, Fe with mixtures of Co-Mo, Ni-Mo and Ni-W preferred.

The metals are employed as oxides or sulphides. Examples of

25 porous material suitable as support include alumina, silica-alumina, alumina-titania, natural and synthetic molecular sieves and mixtures hereof with the alumina and silica-alumina being preferred.

The catalyst used in the posttreatment reactor may be any
catalyst used for hydrotreating vacuum distillate streams.
Preferred catalysts are Ni-Mo, Co-Mo and Ni-W on alumina.
The active metal on the catalyst may be either presulphided

5   or in-situ sulphide prior to use by conventional means. The
hydrotreating reactor section may consist of one or more
reactors. Each reactor may have one or more catalyst beds.

The function of the hydrotreating reactor is primarily to

10   reduce product sulphur, nitrogen, CCR and metals. Owing to
the exothermic nature of the desulphurisation reaction, the
outlet temperature is generally higher than the inlet tem-
perature. Some reduction of PAH may be achieved in the hy-
drotreating reactor especially at start of run conditions.

15   As the catalyst activity declines due to the deactivation
by carbonaceous deposits, sintering of the active phase and
other mechanisms, the inlet temperature to the hydrotreat-
ing reactor is raised, resulting in an increased outlet
temperature.

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This will result at some point in an increase in the PAH
content in the effluent of the hydrotreater reactor due to
equilibrium limitations. The temperature at which this oc-
curs will depend on the amount and type of aromatic com-

25   pounds in the oil, and the hydrogen partial pressure in the
unit.

The function of the post-treatment reactor is primarily to
reduce the PAH content, but also to lower the sulphur and

30   nitrogen. The reduction in PAH will result in a reduction
in the product oil density and refractive index (RI) both
of which are desirable. Also reduction in the sulphur and

nitrogen content will be achieved at the conditions in the post-treatment reactor. The present invention is illustrated in the following examples of specific embodiments.

5 **Example 1**

Feedstock A (Table 1) was hydrotreated in a semi-adiabatic pilot plant unit running with an outlet temperature of 405°C – a temperature, which normally is considered as end of run temperature (EOR) conditions and LHSV at 1 (hr^{-1}).

10 The pressure was 50 bar. Pure hydrogen was used as gas. Feedstock A is a mixture of 50% cooker gas oil and 50% straight run vacuum gas oil (SR VGO). Feedstock B (Table 1) was hydrotreated at typical FCC pretreatment conditions in a pilot plant unit at temperature at 400°C (inlet) – 420°C

15 (outlet) temperature, which normally is considered as end of run conditions at LHSV at 1.7 (h^{-1}). The pressure was 50 bar. The feedstock was a pure cracked VGO.

Table 1

Properties of feedstock used in the following Examples:

Properties	Feedstock A	Feedstock B
SG 60/60	0,9279	0,9924
S (wt %)	1,34	3,53
N (wt ppm)	2677	3594
Aromatics (wt%)		
Mono-	17,7	8,36
Di-	9,9	7,29
Tri-	11,4	36,5

Product properties from both of the tests are shown in Ta-

25 ble 2.

Table 2

Properties of products in Example 1:

Properties	Product A	Product B
SG 60/60	0,8920	0,9411
S (wt %)	0,02	0,1905
N (wt ppm)	526	2046
Aromatics (wt%)		
Mono-	31,0	22,6
Di-	7,8	11,3
Tri-	6,7	23,9
Distillation, D2887 (°C)		
5	236	287
10	267	314
30	342	360
50	392	392
70	437	428
90	495	479
95	518	503

Product A contains 14,5 wt% PAH, which would be typical for a product obtained at EOR conditions in a unit where the hydrogen partial inlet pressure is 50 bar, if the feedstock contains more cracked feedstock or DAO (De-Asphalt Oil) the contents will be higher.

Product B contains 35,2 wt% PAH, which is rather high, but typical for cracked feedstocks.

Example 2

Product A from Example 1 is further hydrotreated at lower temperatures at high LHSV. The pressure is 50 bar, which is identical to the pressure at which product A was obtained.

A Ni-Mo on alumina catalyst is used in this test. The results are shown in Table 3.

Table 3.

Properties of products in Example 2:

Temperature (°C)	LHSV (h^{-1})	SG 60/60	S (wt%)	N (wt ppm)	Di-aromatics (wt%)	Tri-aromatics (wt%)	PAH (wt%)
325	6	0,8914	0,0038	505	4,6	5,0	9,6
350	6	0,8911	0,0029	468	4,9	4,9	9,5

As illustrated from the Table 3 there are a remarkable sulphur and nitrogen removal in this low temperature hydrotreatment, and further it is quite obvious that a large amount of the PAH can be removed at a relatively high LHSV during this low temperature posttreatment. Both the sulphur removal and the PAH removal is due to the shift in equilibrium.

Example 3

Product B from Example 1 is further hydrotreated at lower temperatures at different LHSV and temperatures. The pressure is 50 bar, which is identical to the pressure at which product B was obtained. A Ni-Mo on alumina catalyst is also used in this test. The results are shown in Table 4.

Table 4

Properties of products in Example 3:

Temperature (°C)	LHSV (h⁻¹)	SG 60/60	S (wt%)	N (wt ppm)	Di-aromatics (wt%)	Tri-aromatics (wt%)	PAH (wt%)
300	2	0,9369	0,1500	2058	7,7	20,1	27,8
300	4	0,9390	0,1588	2067	10,2	21,3	31,5
300	6	0,9406	0,1618	2080	9,9	21,4	31,6
350	2	0,9335	0,1049	1657	6,6	17,0	23,6
350	4	0,9365	0,1317	1870	9,2	18,1	27,3
350	6	0,9378	0,1442	1877	9,6	19,3	28,9

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Again it is clear that a large amount of the poly-aromatic compounds can be removed at low temperature (and the same pressure) due to the shift in equilibrium. Again there is a significant and important sulphur removal at this low-temperature hydrotreatment.